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Removal of naphthalene present in synthetic waste water using novel G/GO nano sheet synthesized from rice straw: comparative analysis, isotherm and kinetics

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) leads to negative effects towards the environment, which have carcinogenic and mutagenic properties affecting highly human being as well as the aquatic system. In this study, the main aim was to investigate the percentage removal of one of the PAHs i.e. naphthalene using (G) and (GO). Initially the Graphene Oxide was synthesized from rice straw obtained from local market of West Bengal. Prepared adsorbent was characterized by SEM, XRD, FTIR analysis. Removal efficiency of the synthesized graphene and graphene oxide at varying conditions like adsorbent dose, temperature, were studied. After certain interval, definite amount of samples were taken out, centrifuged and were analyzed using UV-visible spectrophotometer and HPLC. Higher removal at these condition was obtained at pH 7, temperature 30°C, and adsorbent dose 2 g/L for GO and at pH 6, temperature 30°C, and adsorbent dose 2 g/L for G. Maximum percentage removal was found to be 85% and 65% for G and GO respectively. Adsorption isotherm data were analyzed by Langmuir and Freundlich isotherm models and Langmuir isotherm was found to be best fitted for both G and GO. The process was found to follow the pseudo-second order kinetics in each cases.

Introduction

Now-a -days, one of the most alarming problems around the world is the water pollution. This is because of the pollutants which are directly or indirectly discharge into the rivers. Pollutions in water of river or seas affects all the living bodies present in water. Organic compounds characteristic depends on its size, shape, structure and functional groups presents in it and which determines its toxicity. Poly aromatic hydrocarbons (PAHs) are organic compounds containing only carbon and hydrogen, composed of multiple aromatic rings (containing delocalized π electrons) [1-3]. PAHs have fused aromatic rings, that is, rings that share one or more sides. PAHs are very widespread organic pollutants. Main source of PAH is in petroleum and oil Industry. PAH pollution occurs due to a leakage of oil either from ground water or from above ground storage.

A simplest form of PAHs is Naphthalene ($C_{10}H_8$). It is a white crystalline solid which has characteristic order detectable at very low concentration. Naphthalene is a polycyclic aromatic hydrocarbon consisting of fused pair of benzene ring [4]. One of the most common disease due to expose of large amount of naphthalene is hemolytic anemia mainly in children often ingest mothballs of naphthalene of deodorants blocks containing naphthalene. Naphthalene may damage or destroy red blood cells in human blood causing a severe anemia. The National Industrial for Occupational Safety and health has said a limit for an 8 hour time weighted average as well as a short term exposure which are 10 mg/L and 15 mg/L respectively. So naphthalene disposal through waste water should be checked before discharge.

There is a number of different techniques to remove naphthalene from waste water such as solvent extraction, membrane separation, and adsorption [5-6]. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of solid, and become bounds by physical and/or chemical interactions [7-8]. So adsorption has become one of the best alternative treatment techniques for waste water organic pollutants.

Most of the adsorbent containing either expensive or have low removal efficiency. Activated carbon is among those promising adsorbent which although have high treatment efficiencies but is very costly [9-12]. So researchers are engaged in search of an adsorbent which can fulfill both the conditions of high treatment efficiency and low manufacturing cost. Graphene is newly emerging member of carbon materials The Graphene Oxide (GO) is precursor of graphene and retain much of the properties of graphene [13-15], it is generally obtained through a strong oxidation of graphite by modified Hummer's method [16-21].

In this study G/GO was prepared using agricultural waste, straw and the removal efficiency of naphthalene is examined from its aqueous solution.

Materials and methods

Reagents

The reactants used in this study were naphthalene ($C_{10}H_8$) as the adsorbate, sodium hydroxide (NaOH), hydrochloric acid (HCl) 37%, and distilled water. Straw was collected from local rice mill West Bengal

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India. Other reactants used for preparation of graphene oxide such as potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4, 98 wt.%), hydrochloric acid (HCl, 36 wt.%), hydrogen peroxide(H_2O_2, 30 wt.%) were purchased from Merck Germany. All the chemicals were of analytical grade. Rice straw was collected from agricultural field of West Bengal and was washed with deionized water and dried at 60C temperature and was stored in a container for future use.

Synthesis of graphene oxide

GO was prepared using the modified Hummer's method. Briefly, 10 g of carbon compounds obtained from rice straw in a high temperature muffle furnace at 500 C temperature was placed in a flatted neck in 500 mL Erlenmeyer flask. Then, 100 ml of concentrated H_2SO_4 was added with continuous stirring keeping in an ice-water bath, and fixed amount of $KMnO_4$ was slowly added. Stirring was continued for 30minutes in the ice-water bath. Then 75 ml distilled water was added to it and was placed in an incubator shaker at 45°C for 3 hours. The reaction was terminated by adding 100 ml distilled water and 75 ml H_2O_2 aqueous solution. The yellow slurry was gained. The slurry was placed in a digital ultrasonic cleaner for 15 minutes to get uniform particle size. Finally the slurry was filtered through a filter paper and was washed repeatedly with the deionized water, GO and the strongacid filtrate were obtained. The GO was dried in hot air oven at 60°C for 10 hours.

Synthesis of graphene

For the graphene synthesis the fixed amount of GO was added in 100 ml distilled water with constant stirring. After that hydrazine hydrate was added to it. After 1 hour the slurry was filtered through a filter paper and dried in hot air oven at 60°C for 6 hour.

Adsorbate preparation

Analytical grade of naphthalene ($C_{10}H_8$) was used for preparing the naphthalene solution for the purpose of the experiment. Predetermined amount of naphthalene dissolved in distilled water without adjusting the pH which is then store in volumetric flask. The desired concentrations of working solution were obtained by diluting the stock solution successively.

Batch studies

Batch adsorption studies were performed to compare the removal of naphthalene from aqueous solution using G and GO. In 250 ml Erlenmeyer flask, 100 ml solution of known concentration of naphthalene was taken and then a predetermined amount of adsorbent was added to it at 140 rpm in shaker. At different time interval the sample was collected and centrifuged at 10000 rpm for 10 min. Then supernatant was collected and was analyzed in UV-visible spectrophotometer (Lambda 25 Perkin elmer) and High Performance Liquid Chromatography (HPLC). All the experiments were repeated twice and average values has been taken. The percentage of naphthalene removal was calculated for each run by the following equation:

$$\% \text{ Removal}=(C_o-C_e)/C_o \times 100$$

Where, C_o and C_e are the initial and final concentrations of naphthalene in the solution in mg/L. The naphthalene uptake capacity for G and GO was calculated using equation:

$$Qe=(C_o-C_e)\ V/m$$

Results and discussions

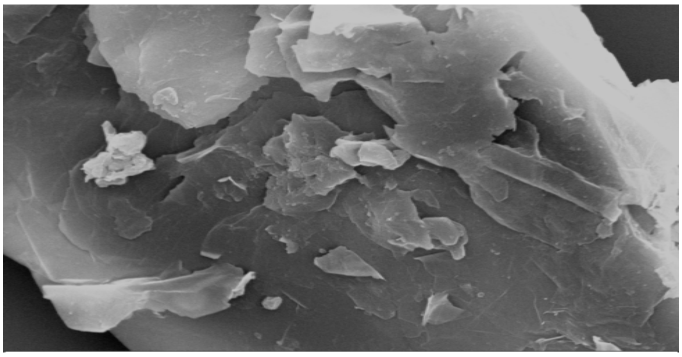

Figure 1a. SEM image of G after adsorption.

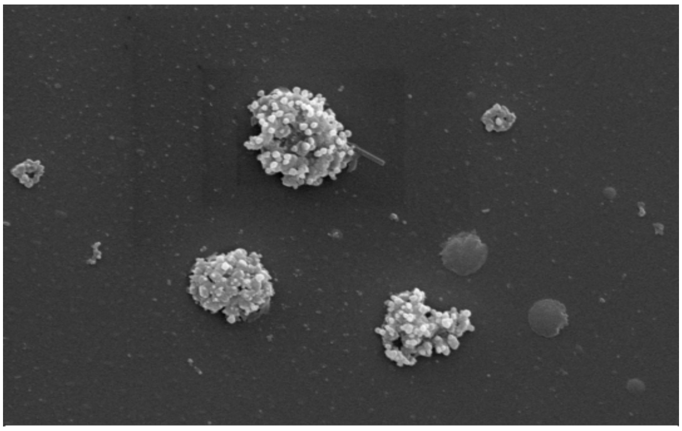

Figure 1b. SEM image of GO after adsorption.

Characterization of the adsorbent

The G and GO prepared from the straw were characterized by SEM (scanning electron microscopy), XRD (X-ray diffraction), FTIR (Fourier transform infrared spectroscopy). The SEM analysis was done to study the morphological structure of adsorbent to study the roughness and smoothness of the surface. The XRD analysis was carried out to investigate the intermolecular distance of the prepared sample, from the FTIR spectroscopy the functional group present on the adsorbent surface was determine. From the figure I 1t was observed that G has thin paper like and GO flower like structure. The detailed analysis of characterization (SEM, XRD, FTIR) is similar as reported in previous study [22].

Effect of adsorbent dose

The effect of adsorbent dose on the removal of naphthalene by G and GO is shown in the Figure 2. Adsorbent dose was varied over a range of 0.05-2 g/L keeping other parameters constant. The percentage of the naphthalene removal increased with an increased adsorbent dose. It was observed that the adsorption efficiency of G is better than that of GO. The higher adsorption of naphthalene on G was mainly attributed to the π-π interaction. Compared to G, GO had lesser π-electron density and more O-containing functional groups [22]. The positive correlation between adsorbent dose and naphthalene removal can be related to an involvement of the adsorbent surface area and also an increment to the availability of more adsorption sites.

Effect of temperature

Temperature determines whether a process is exothermic or

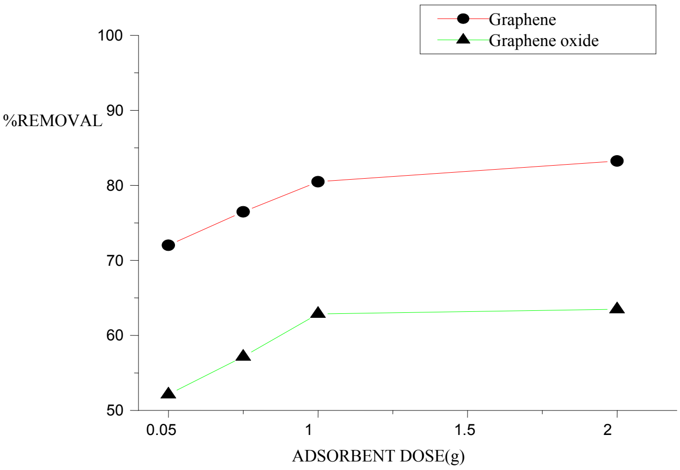

Figure 2. Plot of percentage removal of naphthalene *vs*. adsorbent dose.

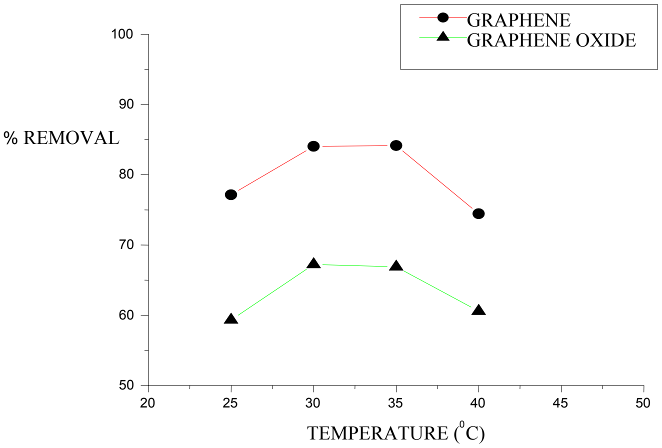

Figure 3. Plot of percentage removal of naphthalene *vs*. temperature for G and GO.

endothermic in nature. It has been previously reported that increased adsorption efficiency of an adsorbent with a corresponding increase in temperature indicates that the process is endothermic in nature [15,16]. The effect of temperature on the percentage removal of naphthalene was studied in the temperature range of 298-313 K and the resultant naphthalene removal is shown in Figure 3. In this present study the maximum removal was obtained at 303 K for G beyond which decreased percentage removal of naphthalene with a corresponding rise in temperature was noted. The same trend was observed for the GO, but removal efficiency was less compared to G. At higher temperature the weakening of the adsorptive forces between the active sites on the adsorbent and the naphthalene species may be considered as a probable explanation of the observed phenomenon.

Effect of pH

The pH of the solution has an important effect on the process of naphthalene adsorption as the ionized naphthalene molecules impart electrostatic charges whose magnitude is controlled by pH of the medium. As a result the adsorption rate varies with the pH of an aqueous medium. Figure 4 shows the effect of pH on the removal efficiency of naphthalene exerted at different pH conditions ranging from 2-10. The best result was obtained at neutral pH (pH 7). In comparative study G shows maximum removal efficiency of naphthalene at pH 7 (82%) whereas in case of GO the maximum removal efficiency of naphthalene to be (60%) at pH 7.

Isotherm model

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquidphase and that on the adsorbent surface at a given condition.

To describe the adsorption equilibrium data we used Langmuir and Freundlich models.

Langmuir:

$$C_e/q_e = C_e/q_m + 1/K_L q_m$$

Freundlich :

$$\log q_e = \log K_F + (1/n)\log C_e$$

where, *qe* (mg g^{-1}) and *Ce* (mg L^{-1}) are the solid phase concentration and the liquid-phase concentration of naphthalene at equilibrium, respectively, *qm* (mg g^{-1}) is the maximum adsorption capacity, K_L (L mg^{-1}) is the Langmuir constant, *K*F (mg g^{-1}) (L mg^{-1})1/*n* is the Freundlich constant related to sorption capacity, *n* is the heterogeneity factor.

For Langmuir model, C_e was plotted against C_e/q_e (Figure 4). The

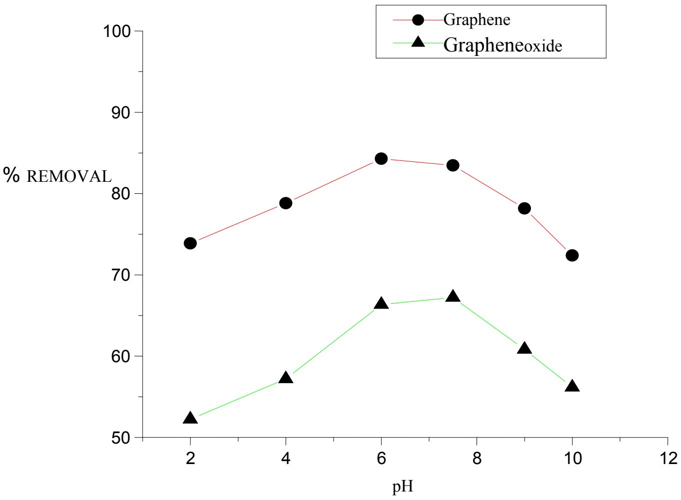

Figure 4. Plot of percentage removal of naphthalene *vs*. Ph.

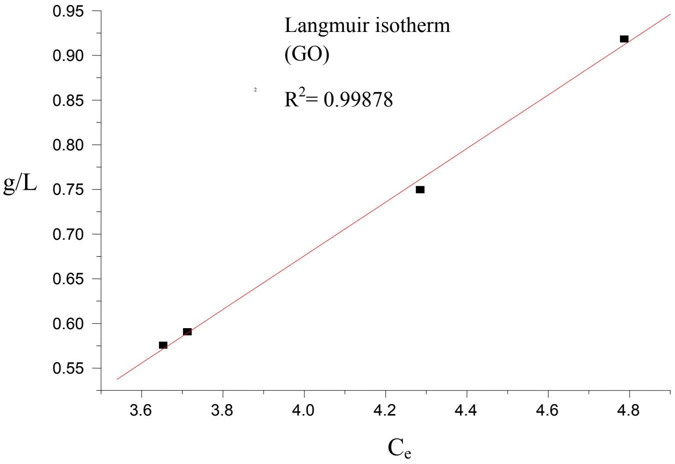

Figure 5. Langmuir isotherm (GO).

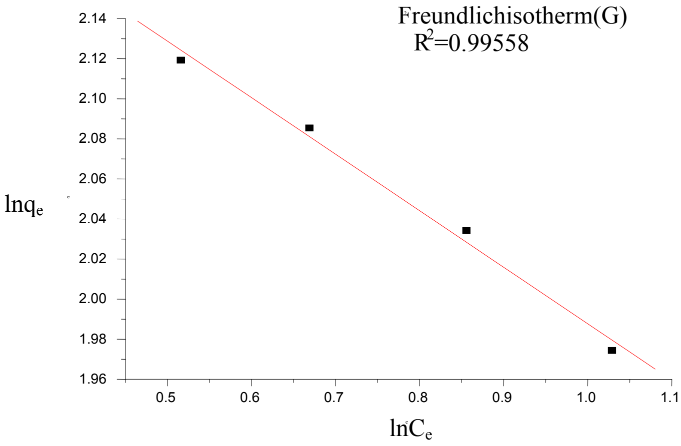

Figure 6. Freundlich isotherm (G).

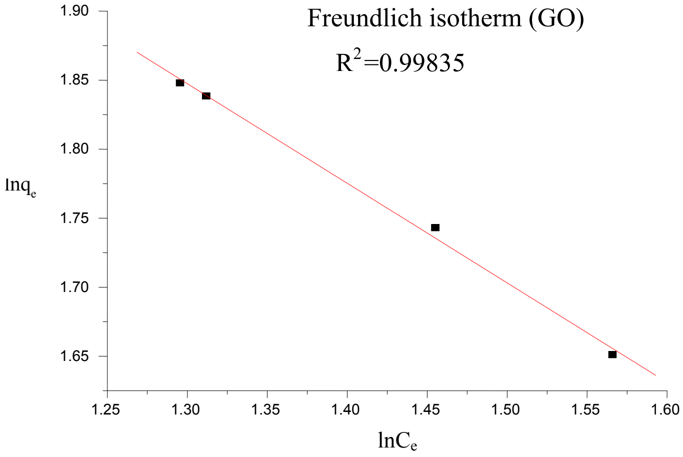

Figure 7. Freundlich isotherms (GO).

Table 1. The values of isotherm constant (G).

Isotherm	Parameter	Values	Isotherm	Parameter	Values
Langmuir	q_m (mg g^{-1})	5.9880	Freundlich	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	9.9046
	K_L(L mg^{-1})	2.0617		1/n	0.1337
	R^2	0.99915		R^2	0.99558

Table 2. The values of isotherm constant (GO).

Isotherm	Parameter	Values	Isotherm	Parameter	Values
Langmuir	q_m (mg g^{-1})	3.3308	Freundlich	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	16.2079
	K_L(L mg^{-1})	0.57161		1/n	1.38587
	R^2	0.99878		R^2	0.99835

Langmuir isotherm showed good fit to the experimental data with high correlation coefficients.

For Freundlichmodel, $\ln q_e$ was plotted against $\ln C_e$ (Figure 5) for the determination of the values of k_L and q_m from the slope and intercept of the plot respectively. The values of K_F and $1/n$ were obtained from the intercept and the slope of the plot.

`The values of constants of Langmuir and Freundlich model are presented in tabulated form (Table 1). The values of q_e were calculated from the constants and were compared (Table 2),

The value of $1/n$ gives a measure of favorability of adsorption. The values of $1/n$ <1 represent a favorable adsorption. In this study, the value of 1/n showed <1, so it can be inferred beneficial adsorption by G and Go both. The value of correlation coefficient was found to be higher for Langmuir model in each cases. So it can be inferred that the Langmuir adsorption model best represents the experimental values confirming that the adsorption is monolayer.

Kinetics

To study the kinetics adsorption model pseudo first and second order models was considered.

Pseudo-first-order: $\log(q_e - q_t) = \log q_e - k1/2.303\ t$

Pseudo-second-order: $t/qt = 1/k^2 q_e^2 + 1/q_e t$

Where qt and qe are the amount of dye adsorbed at time t and at equilibrium (mg g^{-1}), $k1$ (min^{-1}) is the pseudo first-order rate constant and q_t, q_e are the amount of naphthalene adsorbed at time t and at equilibrium (mg g^{-1}) respectively, k_2(g mg^{-1} min^{-1}) is the pseudo-second-order rate constant. t/qt values were plotted against t for G (Figure 8) and for GO (Figure 9). The correlation coefficient was found to be higher for second order. The values of the constants for the second order for G (Table 3) and for GO (Table 4) are shown in tabulated form.

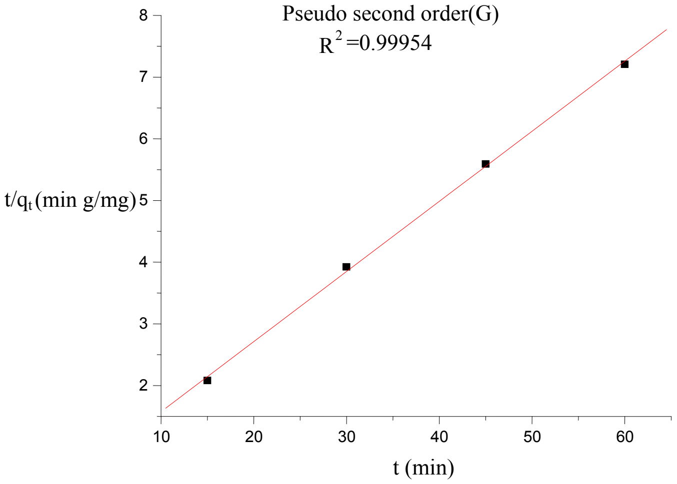

Figure 8. Pseudo second order kinetics model (G).

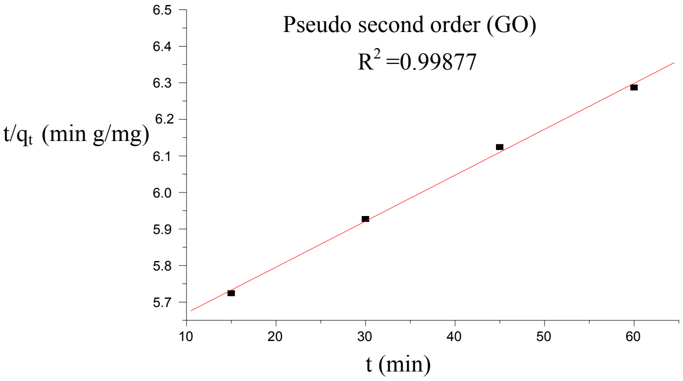

Figure 9. Pseudo second order model (GO).

Table 3. The values of kinetics model constant for G.

Kinetics	Parameters	Values
Pseudo 2nd order	q_e(mg g^{-1})	8.8496
	k_2 (g mg^{-1} min^{-1})	2.85×10^{-5}
	R^2	0.99954

Table 4. The values of kinetics model constant for GO.

Kinetics	Parameters	Values
Pseudo 2nd order	q_e(mg g^{-1})	7.9554
	k_2 (g mg^{-1} min^{-1})	2.902×10^{-2}
	R^2	0.99877

Conclusion

The present investigation showed that the graphene and graphene oxide produced from rice straw are adsorbents for the removal of naphthalene from its aqueous solutions. The naphthalene was found to adsorb strongly on the surface of the adsorbents synthesized. Batch studies showed the better acceptance of graphene over graphene oxide. G shows the better adsorption than GO. The higher adsorption of naphthalene on G was mainly attributed to the π-π interaction. Compared to G, GO has lesser π-electron density and more O-containing functional groups. Adsorption isotherms studies showed better acceptability of Langmuir model. The process was found to follow the pseudo second order kinetics model.

Acknowledgments

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